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STACKED PHOTOVOLTAIC ELEMENT

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8

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[Name of the Document] Specification
[Title of the Invention] Stacked Photovoltaic Element
[Claim(s)]

[Claim 1] A stacked photovoltaic element characterized by comprising a plurality of unit photovoltaic elements each composed of a pn- or pin-junction, connected to each other in series, wherein a zinc oxide layer is provided at least one position between the unit photovoltaic elements, and the zinc oxide layer has resitivity varying in a thickness direction thereof.

[Claim 2] The stacked photovoltaic element

according to Claim 1, characterized in that zinc oxide of the zinc oxide layer on a side of being in contact with a p-layer has a higher resistivity than that on a side of being in contact with an n-layer.

[Claim 3] The stacked photovoltaic element

20 according to Claim 2, characterized in that a

resistivity of the zinc oxide continuously decreases in

the zinc oxide layer from a side of the zinc oxide

layer in contact with the p-layer towards a side of the

zinc oxide layer in contact with the n-layer.

[Claim 4] The stacked photovoltaic element according to any one of Claims 1 to 3, characterized in that a resitivity of zinc oxide of the zinc oxide layer

is $2\times10^{\circ}$ Ω cm or more and $5\times10^{\circ}$ Ω cm or less.

[Claim 5] The stacked photovoltaic element according to any one of Claims 1 to 4, characterized in that a high resistant portion of zinc oxide of the zinc oxide layer has $5\times10^2~\Omega cm$ or more and $5\times10^3~\Omega cm$ or less.

[Claim 6] The stacked photovoltaic element according to any one of Claims 1 to 5, characterized in that at least one of the plurality of the unit photovoltaic elements has a pin-junction comprising an i-type layer composed of amorphous Si:H.

[Claim 7] The stacked photovoltaic element according to any one of Claims 1 to 5, characterized in that at least one of the plurality of the unit photovoltaic elements has a pin-junction comprising an

[Claim 8] The stacked photovoltaic element according to any one of Claims 1 to 5, characterized in that at least one of the plurality of the unit

20 photovoltaic elements has a pin-junction comprising an i-type layer composed of single-crystalline or polycrystalline Si.

i-type layer composed of microcrystalline Si.

[Detailed Description of the Invention]
[0001]

25 [Field of the Invention]

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The present invention relates to a stacked photovoltaic element comprising at least two power-

generating function units.

[0002]

[Prior Art]

A photovoltaic element is a device which converts 5 incident light energy into electric energy. A solar cell is a photovoltaic element which converts solar rays as white light into electric energy. It is characterized by efficiently converting light over a wide wavelength range into electric energy. It is necessary to efficiently absorb light over a wide 10 wavelength range in order to achieve a high conversion efficiency. A stacked photovoltaic element, which is formed by stacking having a semiconductor layer having a different band gap from each other as the photoactive 15 layer is known as a solution. This stacked photovoltaic element has one element having a semiconductor of relatively larger band gap on a light incident side, and another element having a semiconductor of relatively smaller band gap in this order from the light incident side, the former 20 absorbing light of shorter wavelengths with large energy and the latter absorbing light of longer wavelengths with small energy which the former transmits. The stacked photovoltaic element, therefore, can more efficiently absorb and utilize 25 light over a wider wavelength range. [0003]

It is essential to provide each photovoltaic element with light of a wavelength in a range suitable for that element, because a wavelength range of incident light which each photovoltaic element can 5 utilize is restricted depending on the band gap of a semiconductor used as the photoactive layer for that element. In other words, photon cannot be absorbed by the semiconductor when photon has lower energy than the band gap of the semiconductor. In such a case, it only passes through the semiconductor without being 10 utilized. On the other hand, photon having higher energy than the band gap of the semiconductor cannot be fully utilized although it can be absorbed, because potential energy of electron which can be produced when 15 the electron is excited is limited by magnitude of the band gap, whereby the difference between the band gap energy and photon energy cannot be utilized. In other words, it is essential to design a stacked photovoltaic element to selectively introduce light of shorter wavelength range into a photovoltaic element on the 20 incident light side and light of longer wavelength range into another photovoltaic element arranged under the above element.

One of the known solutions is to provide a transparent electroconductive film as a light-reflecting layer between these photovoltaic elements.

[0004]

For example, Patent Document 1 or Non-patent Document 1 disclose a method for providing an electroconductive intermediate layer each between the elements which reflects light of shorter wavelength and transmit light 5 of longer wavelength. Patent Document 2 discloses a method for adjusting the thickness of a selective reflection layer in such a way to increase electric current flowing through a photovoltaic element on the incident light side by setting its peak reflectivity to 10 the maximum wavelength of spectral sensitivity of the photovoltaic element on the incident light side. Patent Document 3 discloses a method for enhancing efficiency of a stacked photovoltaic element by a selective reflection layer of stacked structure having 15 a higher reflectivity for the shorter wavelength range which the upper photoelectron conversion layer can absorb more easily, and a lower reflectivity for the longer wavelength range which the lower photoelectron conversion layer can absorb more easily for transmission. Each of these techniques uses a 20 dielectric layer of SnO_2 , ZnO, ITO or the like as the selective reflection layer, to prevent light of short wavelength, which should be absorbed by the photovoltaic element on the incident light side, from being absorbed by the lower photovoltaic element and 25 thereby to enhance conversion efficiency of the photovoltaic element on the incident light side.

[0005]

[Patent Document 1]

Japanese Patent Application Laid-Open No. S63-77167

5 [Patent Document 2]

Japanese Patent Application Laid-Open No. H2-237172

[Patent Document 3]

Japanese Patent Application Laid-Open No. 2001-10 308354

[Non-patent Document 1]

Kenji Yamamoto, "Thin-film polycrystalline silicon solar cell", Applied Physics, The Japan Society of Applied Physics, May, 2002, Vol.71, No.5, p.524 to 527

15 [0006]

[Problem to be Solved by the Invention]

On the other hand, the following problems occur when the above-described electroconductive reflection layer is provided as the intermediate layer.

20 [0007]

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A photovoltaic element of large area, comprising unit elements stacked on each other in series, e.g., as shown in Fig. 1, has electrical defects within the element, resulting from dust generated during the deposition step, or irregularities or foreign matter on the surface of a substrate. In Fig. 1, numeral 100 denotes the stacked photovoltaic element; 101:

substrate, 102: second photovoltaic element, 103: zinc oxide layer, 104: first photovoltaic element, 105: electroconductive layer as transparent electrode, 106: short circuit in the second photovoltaic element, and 5 107: short circuit in the first photovoltaic element. The electrical defects inevitably associated with the large area deteriorate the element characteristics resulting from decreased shunt resistance and fill factor (FF). One of the effective means to solve these 10 problems is a method (passivation) in which a photovoltaic element is normally dipped in an electrolytic solution and an electric current is passed through it to selectively remove a part of an electroconductive layer outside of an electric defect. 15 However, for a stacked photovoltaic element comprising a lower photovoltaic element layer, an intermediate layer, an upper photovoltaic element layer and an electroconductive layer on a substrate, the above procedure can partly remove the electroconductive layer 105 on the first photovoltaic element layer as the 20 upper layer containing the defect 107, but cannot remove the intermediate layer 103 on the second photovoltaic element layer as the lower layer containing the defect 106. As a result, short-circuit current flows through the defect in the lower layer to 25 decrease electromotive force of the lower photovoltaic element. Short-circuit current cannot be effectively

prevented from spreading into the intermediate layer for various reasons. In particular the intermediate layer should have a certain thickness to function as the reflection layer, and should satisfy the other 5 considerations, e.g., compatibility with the semiconductor layers with which it is in contact on both sides and series resistance. These requirements limit a range in which the resistivity of the materials can be adjusted. Moreover, additional junctions 10 generated between the photovoltaic elements and an intermediate layer of a different material therebetween inevitably deteriorate characteristics which are accompanied by decreased FF. Still more, a plurality of layers inserted to prevent a reduced shunt 15 resistance further increase junction number, thus further aggravating the interfacial problems. [8000]

As discussed above, incorporation of an intermediate layer as a selective reflection layer for increasing photocurrent involves the adverse effect of decreased electromotive force of the photovoltaic element.

[0009]

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The present invention is to provide a photovoltaic
25 element exhibiting a high conversion efficiency
realized by producing large photocurrent without
causing decreased electromotive force.

[0010]

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[Means for Solving the Problem]

In order to achieve the object mentioned above, a stacked photovoltaic element according to the present invention is characterized by comprising a plurality of unit photovoltaic elements each composed of a pn- or pin-junction, connected to each other in series, wherein at least a zinc oxide layer is provided at least one position between the unit photovoltaic elements, and the zinc oxide layer has resitivity varying in the thickness direction.

[0011]

Zinc oxide on a side of being in contact with a player of the pn- or pin-junction has a higher resistivity than that on a side of being in contact with an n-layer of the pn- or pin-junction in the zinc oxide layer.

[0012]

The resistivity of zinc oxide continuously

20 decreases from the p-layer side towards the n-layer side.

[0013]

The resitivity of zinc oxide is preferably $2\times10^{\circ}$ Ω cm or more and 5×10^{3} Ω cm or less.

25 [0014]

The highest resistant portion of zinc oxide preferably has $5\times10^2~\Omega cm$ or more and $5\times10^3~\Omega cm$ or less.

[0015]

Of the plurality of the unit photovoltaic elements for the first aspect, at least one unit photovoltaic element has a pin-junction comprising an i-type layer suitably composed of an amorphous Si:H.

[0016]

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Of the plurality of the unit photovoltaic elements for the first aspect, at least one unit photovoltaic element has a pin-junction comprising an i-type layer suitably composed of microcrystalline Si.

[0017]

Of the plurality of the unit photovoltaic elements for the first aspect, at least one unit photovoltaic element has a pin-junction comprising an i-type layer suitably composed of single-crystalline or polycrystalline Si.

[0018]

[Embodiment(s)]

Fig. 3 outlines a cross-sectional structure of the two-layers-stacked photovoltaic element 300 as one embodiment of the present invention. It has on a substrate 301 of a metal or the like which has a reflection layer stacked thereon, the second photovoltaic element 302, second zinc oxide layer 303, first zinc oxide layer 304, first photovoltaic element 305 and transparent electrode 306 stacked in this order. A semiconductor which constitutes the

photoactive section for the first photovoltaic element 305 has a larger band gap than that of a semiconductor which constitutes the photoactive section for the second photovoltaic element 302. This means that the stacked photovoltaic element 300 is designed in such a 5 way that the first photovoltaic element 305 absorbs light in a short wavelength range while the second photovoltaic element 302 absorbs light in a long wavelength range. The first zinc oxide layer 304 and first photovoltaic element 305 have a different 10 refractive index. Therefore, multiple reflection can be created by adjusting the thickness of each layer to efficiently enhance reflectivity in the short wavelength range, and thereby to increase the quantity 15 of light absorbed by the first photovoltaic element The second zinc oxide layer 303 is designed to have a higher resistivity than that of the first zinc oxide layer 304. [0019]

20 Fig. 4 schematically illustrates power-generating operation of the stacked photovoltaic element of the present invention. An electrical defect in the first photovoltaic element acts as a short-circuit current passage. When the electrical defect 402 in the first photovoltaic element 305 is close to the electrical defect 403 in the second photovoltaic element 302, no deterioration of the photovoltaic element

characteristics is caused by these defects, because the transparent electrode 306 is removed by the shunt passivation treatment carried out after the stacked photovoltaic element is assembled. When these defects 5 are apart from each other at a distance, on the other hand, the characteristics may be deteriorated, because of insufficient shunt passivation treatment. Although the first photovoltaic element 305 is provided with the first zinc oxide layer 304 of lower resistivity on the substrate side surface, it is sufficiently thin and 10 causes spread of short-circuit current in the lateral direction to only a limited extent. Therefore, it little deteriorates the characteristics. [0020]

15 On the other hand, in the vicinity of the electrical defect in the second photovoltaic element 302, the electroconductive zinc oxide layer is present, and the defect acts as a short circuit in the photovoltaic element while power is being generated. However, the second photovoltaic element 302 has the 20 second zinc oxide layer 303 of higher resistivity on the surface of the element 302 (upper layer surface), whereby short-circuit current spreads via the first zinc oxide layer 304 of lower resistivity while its spread in the lateral direction is limited. A total 25 thickness of the first zinc oxide layer 304 and second zinc oxide layer 303 is limited to a level suitable for the selective reflection layer, and spread of the short-circuit current can be efficiently prevented by combination of the higher and lower resistivities.
[0021]

5 The electrical polarities at each junction of the stacked structure consisting of the second photovoltaic element, second and first zinc oxide layer and first photovoltaic element provided in this order are, for example, as shown in Fig. 2, a combination of n-10 /n+/n++, i.e., the second zinc oxide layer 202 of the lowest carrier concentration (n-), the first zinc oxide layer 203 of higher carrier concentration (n+) and the n-type semiconductor layer 204 of the first photovoltaic element of the highest carrier 15 concentration (n++) are stacked in this order. In Fig. 2, 201 denotes a substrate, 202: second zinc oxide layer of n- type, 203: first zinc oxide layer of n+ type, 204: first photovoltaic element as the n-type semiconductor layer of n++ type, 205: transparent electrode, 206: second photovoltaic element, 207: 20

[0022]

element.

The n-type zinc oxide layer can have a controlled

25 bulk carrier concentration by the production

conditions. It is considered that light-generating

carrier can be collected more efficiently by increasing

stacked zinc oxide layer, and 208: first photovoltaic

carrier concentration in the n-type zinc oxide layer stepwise or continuously from the p-type semiconductor layer side of the second photovoltaic element towards the n-type semiconductor layer side of the first photovoltaic element, because increasing or decreasing trend of concentration of the carrier of the same polarity is set in one direction including the n-type semiconductor layer of the first photovoltaic element, thereby efficiently connecting these elements to each other at the band junction, although the concept is not fully substantiated.

[0023]

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The zinc oxide layer as the intermediate layer has a higher resitivity, preferably $2\times10^{\circ}$ Ω cm or more and 5×10^3 Ω cm or less for both the first and second zinc 15 oxide layers, than recent zinc oxide layers of which the resitivity has been greatly decreased. intermediate layer having a resistivity in the above range has a lower carrier concentration than that of the n-type semiconductor layer of the first 20 photovoltaic element, conceivably resulting in improved junction. On the other hand, short-circuit current is considered to diffuse in the zinc oxide layer, unless zinc oxide has a resistivity of $5 \times 10^2 \ \Omega \text{cm}$ or more and 5×10^3 Ω cm or less in the high-resitivity portion, to 25 deteriorate the characteristics.

[0024]

The zinc oxide layer preferably transmits at least 50% of light having a wavelength of 800 nm. The wavelength range of solar light which can be effectively utilized by the photovoltaic element is approximately from 300 to 1200 nm in consideration of its spectral pattern. The cell at the upper section of the zinc oxide layer absorbs light of short wavelength, and hence it is preferable for the zinc oxide layer to effectively transmit light of long wavelength.

10 Therefore, it preferably transmits at least 50% of light having a wavelength of 800 nm, which represents the long wavelength.
[0025]

Hereinafter, the embodiments describe example for 15 a solar cell as a stacked photovoltaic element comprising two photovoltaic layers (unit photovoltaic elements), produced by stacking on a substrate, a reflection layer, a photovoltaic element of microcrystalline silicon (hereinafter referred to as the "bottom cell"), an intermediate layer of zinc oxide 20 and a photovoltaic element of amorphous silicon (hereinafter referred to as the "top cell") in this order from the substrate side. However, the present invention is by no means limited to the above structure, and the number of the photovoltaic elements 25 may be increased as required.

[0026]

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Next, each component for the present invention is described in detail.

[0027]

[Substrate]

5 The material for the substrate which constitutes the stacked photovoltaic element of the present invention is not limited. It may be an electroconductive or insulating material of any type. The electroconductive materials include metals, e.g., 10 plated steel, NiCr, stainless steel, Al, Cr, Mo, Au, Nb, Ta, V, Ti, Pt, Pb, Sn and an alloy thereof. insulating materials include synthetic resins, e.g., polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, 15 polyvinylidene chloride, polystyrene and polyamide; and glass, ceramics and paper. The particularly preferable materials are stainless steel as the metal substrate, and glass, ceramics and polyimide as the insulating substrate. A transparent, insulating substrate is used for the stacked photovoltaic element with incident 20 light entering from the substrate side, and glass is suitable for the substrate. [0028]

The substrate surface may be smooth or of

25 irregular texture with irregularities having the

maximum height of 0.1 to 1.0 µm. A stainless steel

substrate may have a surface of irregular texture by

etching with an acidic solution.
[0029]

Thickness of the substrate may be adequately set to give a desired stacked photovoltaic element by stacking the layers one on another as intended. When the stacked photovoltaic element is required to be flexible, it may be as thin as possible so long as it can sufficiently work as a support. However, it normally has a thickness of 10 µm or more in consideration of production, handling and mechanical strength.

[0030]

light.

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[Reflection Layer]

The reflection layer for the stacked photovoltaic 15 element of the present invention comprises of a metal reflection layer and an increased reflection layer. The metal reflection layer is made of a deposited film of a metal which has a high reflectivity of light from the visible to near-infrared ray, e.g., Ag, Al, Cu and an alloy thereof. It is suitably formed by, e.g., 20 vacuum evaporation, sputtering or electrolytic deposition from an aqueous solution. It is preferably 10 to 5000 nm thick. It is preferably provided with irregularities on the surface for irregular reflection. It is also preferably provided with an increased 25 reflectance layer to increase quantity of reflected

[0031]

The materials for the increased reflectance layer include ZnO, SnO₂, In₂O₃, ITO, TiO₂, CdO, Cd₂SnO₄, Bi₂O₃, MoO_3 and Na_xWO_3 . The increased reflectance layer is 5 suitably formed by vacuum evaporation, sputtering, electrolytic deposition, CVD, spraying, spin-on, dipping or the like of the above material. thickness is preferably 50 nm to 10 μm , although the optimum thickness varies depending on inherent 10 reflectivity of the material used. The increased reflectance layer is preferably provided with irregularities on the surface for increasing light scattering. For example, in the sputtering method sputtering conditions may be selected to provide 15 irregularities based on the grain boundaries. [0032]

[Photovoltaic Laver]

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The semiconductors useful for the stacked photovoltaic element of the present invention include single-crystalline, poly-crystalline, microcrystalline and amorphous materials of IV, III-V, II-VI, I-III-VI2 groups. The IV group materials include C, Si and Ge and an alloy thereof, III-V group materials AlAs, AlSb, GaN, GaP, GaAs, GaSb, InP and InAs, II-VI group materials ZnSe, ZnS, ZnTe, CdS, CdSe, CdTe and Cu₂S, 25 and I-III-VI2 group materials CuInSe2. Of these, silicon-based semiconductors are more preferable.

single-crystalline, poly-crystalline, microcrystalline and amorphous semiconductors are suitably used.
[0033]

The photovoltaic layer for the stacked

5 photovoltaic element of the present invention contains a pn- or pin-junction.

[0034]

The stacked photovoltaic element of the present invention comprises at least two photovoltaic layers.

The semiconductors for these photovoltaic layers may be the same or different material. However, in the preferable structure, a photovoltaic layer using a semiconductor which can more efficiently absorb light of shorter wavelengths and another photovoltaic layer using a semiconductor which can more efficiently absorb light of longer wavelengths are stacked in this order from the incident light side, because light of shorter wavelength is more easily absorbed.

[0035]

20 [Zinc Oxide Layer]

The stacked photovoltaic element of the present invention has an intermediate layer composed of zinc oxide in at least one position between the photovoltaic layers (unit photovoltaic elements).

25 [0036]

The zinc oxide layer for the present invention can be suitably formed by vacuum evaporation, DC magnetron

sputtering, RF magnetron sputtering, electrolytic deposition, electroless plating, CVD, MOCVD, spraying, spin-on, dipping, sol-gel process or the like. The generally known dopants for adjusting its resistivity include Al, B, Ga and In. The other known dopants include tetravalent metals, e.g., Si, Ge, Ti and Zr. When a common vacuum evaporation or sputtering method is employed, zinc oxide (target or the like) may be sintered after previously adding the dopant at a desired content to zinc oxide.

[0037]

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The zinc oxide layer has a varying reflectivity to reflect more light having a wavelength shorter than the wavelength λm , at which the second photovoltaic element attains the highest spectral characteristics, and to reflect less light having a wavelength longer than the wavelength λm , in order to efficiently convert energy of incident light over an entire wavelength range. The zinc oxide layer preferably has a transmittance of 80% or more, to efficiently utilize incident light.

The zinc oxide layer for the present invention has a resistivity varying in the thickness direction to prevent deteriorated element characteristics caused by shunt, as the problem involved in the conventional layer, while keeping its function as a selective reflection film. Its resitivity is preferably $2 \times 10^{\circ}$

 Ω cm or more and 5×10^3 Ω cm or less. The high resistivity portion of the zinc oxide layer is preferably 5×10^2 Ω cm or more and 5×10^3 Ω cm or less. Its thickness is preferably 0.2 to 2μ m in consideration of its reflectivity, series resistance and irregularities on the surface.

[0039]

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[Transparent Electrode]

The materials for the transparent electrode for

the stacked photovoltaic element of the present
invention include indium oxide, tin oxide, indium-tin
oxide or zinc oxide. The transparent electrode is
formed by sputtering, vacuum evaporation, chemical
vapor deposition, ion plating, ion beam or ion beam

sputtering. It may be also formed by electrolytic
deposition or immersion in an aqueous solution of a
metallic ion, e.g., that containing nitric, acetic or
ammonia group. It preferably has a sufficient
thickness to satisfy the requirements as an

antireflection film.

[0040]

25

[Examples]

The examples as the preferred embodiments of the present invention are described in detail by referring to the attached drawings, however, the present invention is not limited to these embodiments.

[0041]

[Example 1]

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In Example 1, the stacked photovoltaic element having the pin-type second photovoltaic element 302 with the i-layer of intrinsic microcrystalline Si, pin-type first photovoltaic element 305 with the i-layer of intrinsic amorphous Si:H and the intermediate layer of zinc oxide (refer to Fig. 3) was produced.

[0042]

The substrate 301, 45 mm square and 0.15 mm thick,

10 was of flat stainless steel (SUS 430), commonly
referred to as BA-finished one. It was put in a
commercial DC magnetron sputtering unit (not shown),
which was evacuated to a pressure of 10⁻³ Pa or less.
[0043]

15 Argon was blown into the unit at 30 cm³/min (normal conditions) to keep pressure inside at 2×10⁻¹
Pa. A DC power of 120 W was applied to an aluminum target (diameter: 6 inches) for 90 seconds to form a thin film of aluminum with a thickness of 70 nm on the 20 substrate, while the substrate was kept unheated. Then, a DC power of 500 W was applied to a zinc oxide target (diameter: 6 inches), after the electrical connection was changed, for 30 minutes to form the reflection layer of zinc oxide with a thickness of 25 about 500 nm, while the substrate was heated at 200°C. [0044]

Fig. 5 schematically illustrates one embodiment of

suitable apparatus for producing a semiconductor layer for the stacked photovoltaic element of the present invention, where the deposited film forming apparatus 500 comprises the following major components; 501: load 5 chamber, 503: chamber for the i-type layer of microcrystalline silicon, 504: RF chamber for the i-type layer of amorphous silicon, 502: RF chamber for the n-type layer, 505: RF chamber for the p-type layer and 506: unload chamber. These chambers are isolated 10 from each other by a gate valve 507, 508, 509, 510 or 511 so that feed gases of the respective chambers are not mixed with each other.

The chamber 503 for the i-type layer of 15 microcrystalline silicon is composed of the heater 512 for heating the substrate and plasma CVD chamber 513. The RF chamber 502 is composed of the heater 514 for depositing the n-type layer and deposition chamber 515 for depositing the n-type layer, the RF chamber 504 the heater 516 for depositing the i-type layer and 20 deposition chamber 517 for depositing the i-type layer, and the RF chamber 505 the heater 518 for depositing the p-type layer and deposition chamber 519 for depositing the p-type layer. The substrate is supported by the substrate holder 521 to run on the 25 rail 520 by a roller driven from an outside power source. In the plasma CVD chamber 513, a microcrystal

is deposited by microwave plasma CVD or VHF plasma CVD. [0046]

The deposited film forming apparatus of the above structure was used to form, as the second photovoltaic element 302, pin-type photovoltaic element whose i-type layer was of intrinsic microcrystalline Si under the deposition conditions given in Table 1 by the following procedure.

[0047]

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10 First, the substrate 301 provided with a reflection layer was set on the substrate holder 521 and then on the rail 520 in the load chamber 501. The load chamber 501 was then evacuated to a vacuum of several hundreds mPa or less.

15 [0048]

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Next, the gate valve 507 was opened, and the substrate holder 521 was moved into the deposition chamber 515 for depositing the n-type layer in the chamber 502, where the n-type layer was deposited to a given thickness using a given feed gas, while the gate valves 507, 508, 509, 510 and 511 were kept closed. The chamber was sufficiently evacuated, and the gate valve 508 was opened to move the substrate holder 521 into the deposition chamber 503. Then the gate valve 508 was closed.

[0049]

The substrate was heated to a given temperature by

the heater 512, a necessary quantity of the feed gas was charged in the chamber, and given microwave or VHF energy was introduced into the deposition chamber 513 which was evacuated to a given vacuum level, to generate a plasma therein to deposit the i-type layer of microcrystalline silicon to a given thickness. The chamber 503 was sufficiently evacuated, and the gate valves 509 and 510 were opened to move the substrate holder 521 from the chamber 503 to the chamber 505.

After the substrate holder 521 was moved into the deposition chamber 519 for depositing the p-type layer in the chamber 505, the substrate was heated to a given temperature by the heater 518. A necessary quantity of the feed gas to deposit the p-type layer was charged into the deposition chamber 519 into which RF energy was introduced to deposit the p-type layer to a given thickness, while the chamber was kept at a given vacuum level.

20 [0051]

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Similarly as in the above, the deposition chamber 519 was sufficiently evacuated, and the gate valve 511 was opened to move the substrate holder 521 into the unload chamber 506. Then, all gate valves were closed and nitrogen gas was charged into the unload chamber 506, and the substrate was cooled with nitrogen gas in the unload chamber 506, while all of the gate valves

were closed. Then, the substrate holder 521 was taken out of the unload chamber 506, after the discharge valve was opened.

[0052]

[Table 1]

[table t]										
		Gas for layer formation					er			
		(cm³/minute under normal					ity			
		conditions)				(W/c	em²)	D		Thickness
				PH ₃	BF ₃			Pressure	Substrate	of layer
		SiH ₄	II	(diluted	(diluted	RF	VHF	(Pa)	temperature(°C)	(nm)
) SIN4	H ₂	to 2%	to 2%	1/1	VUL			
				with H ₂)	with H ₂)					
Second	N2	2	48	0.5		0.04		180	225	20
photovoltaic	12	25	750				0.2	40	250	2000
element	P2	0.025	35		1	1.2		270	165	5

[0053]

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Next, the substrate, on which the layers up to the second photovoltaic element 302 was formed, was removed from the substrate holder 521, and set on the substrate holder 601 in the DC magnetron sputtering apparatus 600 for forming a zinc oxide layer, shown in Fig. 6. Then, the apparatus was evacuated to a pressure of 10^{-3} Pa or less.

[0054]

The substrate holder 601 was electrically 10 insulated, and could keep the photovoltaic element as the sample floated. The apparatus was kept at a pressure of 2×10^{-2} Pa while argon gas was supplied at 50 sccm, and oxygen gas and vaporized H_2O gas were 15 supplied at a rate given in Table 2 within 0.1 to 5 sccm, all via the gas inlet tube 602. The substrate holder 601 was heated by the heater 603 to keep the substrate at 150°C. A DC power of 500 W was applied from the DC power source 605 onto the Al-doped zinc oxide (ZnO) target 604 (diameter: 6 inches) for 10 20 minutes, to deposit the second zinc oxide layer 303 with a thickness of about 0.5 µm on the substrate. target 604 was surrounded by the earth shield 606, to prevent diffusion of the plasma and to stabilize the discharge. At the same time, a quartz substrate (45 by 25 45 mm) was set on the substrate holder to deposit thereon the same layer of zinc oxide for the analysis

of its electrical properties.
[0055]

Next, on each of the zinc oxide layers 303,
Samples A to J given in Table 2 formed on each

5 substrate, the first zinc oxide layer 304 was deposited under the conditions of A to J as given in Table 2. A total of 100 samples were prepared. At the same time, a quartz substrate (45 by 45 mm) was set on the substrate holder to deposit thereon the same layer of zinc oxide for the analysis of its electrical properties.

[0056]

[Table 2]

Sample No.	Oxygen flow rate	${ m H_2O}$ flow rate		
	(sccm)	(sccm)		
А	0.1	10		
В	0.3	10		
С	0.4	10		
D	0.5	10		
E	0.8	10		
F	1.0	10		
G	2.0	5		
Н	5.0	5		
1	10.0	2		
J	15.0	2		

[0057]

Next, the deposited film forming apparatus 500 was

again used to form, on a substrate on which the above intermediate layer (zinc oxide layer) was formed, as the first photovoltaic element 305, pin-type photovoltaic element whose i-type layer was of intrinsic amorphous Si:H under the deposition conditions given in Table 3 by the following procedure. [0058]

First, the n-type layer was deposited under given conditions to a given thickness in a manner similar to that described above. The gate valves 508 and 509 were opened and the substrate holder 521 was moved into the deposition chamber 504, after it was sufficiently evacuated. Then, these valves were closed.

[0059]

The substrate was heated to a given temperature by the heater 516, and a necessary quantity of the feed gas was charged in the chamber. Given RF energy was introduced into the deposition chamber 517, which was evacuated to a given vacuum level, to generate a plasma therein to deposit the i-type layer of amorphous Si:H to a given thickness by adjusting deposition time. The chamber 504 was sufficiently evacuated, and the gate valve 510 was opened to move the substrate holder 521 from the chamber 504 to the chamber 505.

25 [0060]

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10

The p-type layer was deposited to a given thickness in a manner similar to that described above.

[0061]

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Then, the deposition chamber 519 was sufficiently evacuated, and the gate valve 511 was opened to move the substrate holder 521, which carried the substrate provided with the layers up to the first photovoltaic element 305, into the unload chamber 506 also in a manner similar to that described above.

[0062]

Then, the substrate holder 521 was taken out of the unload chamber 506 also in a manner similar to that described above.

[0063]

[Table 3]

[table 1]										
		Gas for layer formation					er			
		(cm³/minute under normal					ity			
		conditions)				(W/c	em²)	D		Thickness
				PH ₃	BF ₃			Pressure	Substrate	of layer
		0,111	TT	(diluted	(diluted	חת	7711	(Pa)	temperature(°C)	(nm)
		SiH ₄	H ₂	to 2%	to 2%	RF	VHF			
				with H ₂)	with H ₂)					
First	N2	2	48	0.5		0.04		180	225	10
photovoltaic	12	2	48			0.04		150	210	500
element	P2	0.025	35		1	1.2		270	165	5

[0064]

Next, the substrate provided with the layers up to the first photovoltaic element 305 was set on the anode surface of a DC magnetron sputtering apparatus, and masked with stainless steel. Indium/tin oxide was sputtered as the transparent electrode onto the substrate in a center area of a 40 by 40 mm using a target of mixed oxide of tin (10% by weight) and indium (90% by weight).

10 [0065]

5

The oxide film was deposited to a 70 nm under the conditions of substrate temperature: 170°C, argon (as an inert gas) flow rate: sccm, oxygen gas flow rate: 0.5 sccm, pressure in the deposition chamber: 300 mPa, power density on the unit target area: 0.2 W/cm² and deposition time: about 100 seconds. Thickness of the film was estimated by the predetermined relationship between thickness and deposition time. The photovoltaic element sample thus prepared was named

20 "Ex. 1".

[0066]

[Comparative Example 1]

A photovoltaic element was prepared in the same manner as in Example 1, except that no zinc oxide layer was placed between the first and second photovoltaic element.

[0067]

25

(Measurement)

First, the electrical characteristics of the zinc oxide layer deposited on the quartz substrate in Example 1 were measured. Resistivity of zinc oxide varies over a wide range (10 digits), and should be 5 evaluated by an analysis system suitable for the resistance varying values. The 2-terminal method generally used for insulators is sensitive to contact resistance, and a resistivity meter (MCP-T600 10 manufactured by Dian Instruments company) based on the 4-terminal method was used, where a constant current was applied by the system including 4 terminals and 4 probes connected in series to measure a potential across and thereby resistivity. The results are given 15 in Table 4. A zinc oxide layer prepared with the target containing a higher content of dopant and smaller quantities of charged O_2 and H_2O had a lower resistivity.

[0068]

[Table 4]

Sample No.	Resistivity (Ωcm)				
A	5.0×10 ⁻¹				
В	3.0×10 ⁰				
С	5.5×10°				
D	1.5×10 ¹				
E	5.5×10 ²				
F	8.5×10 ²				
G	1.4×10 ³				
Н	5.2×10 ³				
I	8.0×10 ³				
J	1.0×10 ⁴				

[0069]

Next, a total of 101 photovoltaic element samples prepared in each of Example 1 and Comparative Example 1 were measured for the current-voltage characteristics while they were irradiated with light under the conditions of AM1.5 spectral pattern and intensity of 100 mW/cm² using an analyzer (YSS-150 manufactured by Yamashita Denso company), and their short-circuit 10 current density Jsc (mA/cm²), open voltage Voc (V) and fill factor FF were estimated based on these characteristics to determine conversion efficiency η(%).

[0070]

Shunt resistance (Rsh) and series resistance (Rs) 15 were also estimated based on the current-voltage

characteristics under a dark condition, where the former was defined as slope near V=0, and the latter as slope of current when it rose up. [0071]

5 The results are given in Tables 5, 6, 7 and 8, respectively.

The zinc oxide layer having a higher resistivity on the second photovoltaic element side and a lower resistivity on the first photovoltaic element side can improve FF level, increase photocurrent and improve 10 conversion efficiency for the stacked photovoltaic element by increasing reflection, reducing shortcircuit current and improving the joint surface. On the other hand, the layer having a reversed combination 15 of resistivity deteriorates in conversion efficiency as the Jsc value decreases. Moreover, the layer having the former resistivity combination exhibits excellent characteristics, when its resistivity is in a range from $2\times10^{\circ}$ Ω cm to 5×10^{3} Ω cm. However, it deteriorates in conversion efficiency when its resistivity is below 20 $2\times10^{\circ}$ Ω cm or the high resistivity portion has $5\times10^{\circ}$ Ω cm or less, resulting in decreased shunt resistance by short-circuit current, which in turn causes decreased FF value and then Jsc level. Resistivity exceeding 5×10^3 Ω cm, on the other hand, slightly reduces the 25 conversion efficiency, resulting from increased series resistance.

[0072]

[Table 5]

Cor	Conversion		First zinc oxide layer										
efi	ficiency	A	В	С	D	E	F	G	H	I	J		
	Comparative Example 1		0.943										
	A	0.971	0.969	0.972	0.973	0.971	0.981	0.978	0.977	0.973	0.972		
	В	0.970	0.972	0.975	0.972	0.976	0.980	0.981	0.982	0.981	0.978		
Second	С	0.985	0.981	0.982	0.983	0.981	0.981	0.982	0.982	0.982	0.980		
zinc	D	0.973	0.980	0.983	0.983	0.984	0.985	0.985	0.986	0.986	0.985		
oxide	E	0.974	0.982	1.105	1.053	1.002	0.988	0.978	0.980	0.990	0.986		
layer	F	0.982	0.990	1.101	1.110	1.058	1.015	0.991	0.992	0.990	0.990		
	G	0.985	0.992	1.102	1.102	1.169	1.140	1.011	0.987	0.991	0.996		
	H	0.983	0.993	1.103	1.110	1.089	1.088	1.090	1.005	0.958	0.980		
	I	0.988	0.990	0.995	0.996	0.998	0.992	0.994	0.993	0.991	0.990		
	J	0.986	0.987	0.991	0.992	0.995	0.991	0.993	0.991	0.990	0.989		

[0073]

[Table 6]

70.0			First zinc oxide layer											
	JSC	A	В	С	D	E	F	G	Н	I	J			
	Comparative Example 1		0.960											
	A	0.971	0.969	0.972	0.973	0.971	0.981	0.978	0.977	0.973	0.972			
	В	0.970	0.972	0.975	0.972	0.976	0.980	0.981	0.982	0.981	0.978			
Second	С	0.985	0.981	0.982	0.983	0.981	0.981	0.982	0.982	0.982	0.980			
zinc	D	0.973	0.980	0.983	0.983	0.984	0.985	0.985	0.986	0.986	0.985			
oxide	E	0.974	0.982	1.105	1.053	1.002	0.988	0.978	0.980	0.990	0.986			
layer	F	0.982	0.990	1.101	1.110	1.058	1.015	0.991	0.992	0.990	0.990			
	G	0.985	0.992	1.102	1.102	1.169	1.140	1.011	0.987	0.991	0.996			
	H	0.983	0.993	1.103	1.110	1.089	1.088	1.090	1.005	0.958	0.980			
	I	0.988	0.990	0.995	0.996	0.998	0.992	0.994	0.993	0.991	0.990			
	J	0.986	0.987	0.991	0.992	0.995	0.991	0.993	0.991	0.990	0.989			

[0074]

[Table 7]

		First zinc oxide layer											
Shunt	resistance	A	В	С	D	E	F	G	Н	I	J		
	A	0.956	0.955	0.960	0.954	0.946	0.952	0.953	0.954	0.956	0.963		
	В	0.963	0.972	0.974	0.978	0.985	0.989	0.988	0.987	0.986	0.990		
	С	0.978	0.979	0.982	0.981	0.984	0.992	0.991	0.993	0.990	0.994		
Second	D	0.985	0.989	0.990	0.992	0.991	0.989	0.992	0.996	0.993	0.994		
zinc	E	1.001	1.000	1.002	1.010	1.005	1.008	1.005	1.010	1.015	1.053		
oxide	F	0.996	0.999	1.003	1.002	1.003	1.010	1.005	1.015	1.045	1.060		
layer	G	0.999	0.996	1.005	1.003	1.020	1.010	1.011	1.022	1.065	1.121		
	H	0.999	1.002	1.004	1.005	1.009	1.015	1.019	1.030	1.089	1.156		
	I	1.001	1.003	1.008	1.006	1.010	1.011	1.069	1.155	1.120	1.188		
	J	1.010	1.011	1.009	1.010	1.011	1.023	1.088	1.145	1.165	1.190		

[0075]

[Table 8]

		First zinc oxide layer											
Series	resistance	A	В	С	D	E	F	G	Н	I	J		
	A	0.989	0.989	0.989	0.992	0.994	0.995	0.999	0.999	1.098	1.200		
	В	0.990	0.991	0.994	0.999	0.999	1.001	1.000	1.002	1.090	1.201		
	С	0.993	0.995	0.998	1.002	1.001	0.998	0.999	1.000	1.082	1.205		
Second	D	0.996	0.996	0.999	0.997	0.989	0.992	1.001	1.003	1.102	1.197		
zinc	E	0.995	0.988	0.996	0.995	1.002	1.003	1.009	1.100	1.152	1.199		
oxide	F	0.993	0.991	0.997	1.020	1.001	1.005	1.012	1.120	1.135	1.140		
layer	G	0.989	0.996	0.999	1.002	1.002	1.005	1.015	1.153	1.190	1.250		
	Н	0.989	0.999	0.999	1.011	1.010	1.010	1.015	1.160	1.203	1.203		
	I	1.025	1.060	1.055	1.068	1.088	1.101	1.105	1.169	1.170	1.201		
	J	1.150	1.155	1.102	1.100	1.111	1.056	1.177	1.188	1.165	1.250		

[0076]

*In the above-described relative series resistance, a larger numeral represents a higher series resistance. The electrical properties deteriorate as series resistance increases.

5 [0077]

[Example 2]

A stacked photovoltaic element was prepared in a manner similar to that for Example 1, by using a pintype photovoltaic element 302 with the i-layer of intrinsic microcrystalline Si as the second photovoltaic element, a pin-type photovoltaic element 305 with the i-layer of intrinsic amorphous Si:H as the first photovoltaic element, and an intermediate layer of zinc oxide (refer to Fig. 3).

15 [0078]

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The zinc oxide layer sample was prepared separately from the photovoltaic element on a quartz substrate, where the same Al-containing target was used, and charge rates of oxygen gas and vaporized H₂O gas were adjusted to have a varying electric conductivity (Table 9). Based on these results, the conditions were found to prepare the zinc oxide layer having resistivity gradually changing in the thickness direction of the layer, so-called graded resistivity.

25 [0079]

The stacked photovoltaic element with the intermediate layer of zinc oxide was prepared in the

same manner as in Example 1, except that the zinc oxide layer was prepared under the conditions given in Table 10, where these conditions were adjusted to give zinc oxide resitivity increasing from the first photovoltaic element side towards the second photovoltaic element side.

[0800]

5

The stacked photovoltaic element samples thus prepared (Ex. 2-1 to 2-5) were evaluated in the same

10 manner as in Example 1. The results are also given in Table 10.

[0081]

[Table 9]

Sample No.	Resistivity (Ωcm)				
A	5.0×10 ⁻¹				
В	5.0×10°				
С	2.5×10 ¹				
D	5.5×10 ¹				
E	5.5×10 ³				
F	5.0×10 ³				
G	7.5×10 ³				

[0082]

[Table 10]

Element No.	Resistivity	Conversion
Element No.	range	efficiency
Ex. 2-1	5.0×10 ⁰ -5.0×10 ³	1.000
Ex. 2-2	5.0×10 ² -5.0×10 ³	1.010
Ex. 2-3	5.0×10°-4.0×10²	0.979
Ex. 2-4	5.0×10 ⁻¹ -1.0×10 ³	0.985
Ex. 2-5	5.0×10°-7.5×10³	0.987

[0083]

It is found also in Example 2 that the zinc oxide layer having a higher resistivity on the second photovoltaic element side and a lower resistivity on the first photovoltaic element side can increase reflection, improve short-circuit current and improve the joint surface of the stacked element, to improve its FF level, photocurrent and conversion efficiency, even when resistivity increases in a graded manner. [0084]

It is also found that the effective resistivity range is $2\times10^{0}~\Omega cm$ or more and $5\times10^{3}~\Omega cm$ or less, and high resistivity range is $5\times10^{2}~\Omega cm$ or more.

15 [0085]

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[Effect of the Invention]

As explained so far, the present invention can provide a stacked photovoltaic element exhibiting a high conversion efficiency realized by efficiently absorbing light over an entire wavelength range of

incident light, reducing short-circuit current flowing an electrical defect and improving juncture between the zinc oxide layer and semiconductor layer.

[Brief Description of the Drawings]

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25

- 5 [Fig. 1] A schematic cross-sectional view showing the structure of a conventional photovoltaic element provided with a zinc oxide layer.
 - [Fig. 2] A schematic cross-sectional view showing the electrical polarities of a part of one embodiment of the stacked photovoltaic element of the present invention.
 - [Fig. 3] A schematic cross-sectional view showing the structure of one embodiment of the stacked photovoltaic element of the present invention.
- 15 [Fig. 4] A schematic cross-sectional view showing the power-generating operation of the stacked photovoltaic element of the present invention.
 - [Fig. 5] A schematic view illustrating one embodiment of a suitable apparatus for producing a semiconductor layer for the stacked photovoltaic element of the present invention.
 - [Fig. 6] A schematic view illustrating one embodiment of a suitable apparatus for producing a zinc oxide layer for the stacked photovoltaic element of the present invention.

[Description of Reference Numerals or Symbols]

100 Stacked photovoltaic element

- 101 Substrate
- 102 Second photovoltaic element
- 103 Zinc oxide layer
- 104 First photovoltaic element
- 5 105 Transparent electrode
 - 106 Short circuit in the second photovoltaic element
 - 107 Short circuit in the first photovoltaic element
 - 200 Stacked photovoltaic element of the present invention
- 10 201 Substrate
 - 202 Second zinc oxide layer showing n- type electrical properties
 - 203 First zinc oxide layer showing n+ type electrical properties
- 15 204 n-type semiconductor of first photovoltaic element showing n++ type electrical properties
 - 205 Transparent electrode
 - 206 Second photovoltaic element
 - 207 Zinc oxide layer
- 20 208 First photovoltaic element
 - 300 Stacked photovoltaic element of the present invention
 - 301 Substrate
 - 302 Second photovoltaic element
- 25 303 Second zinc oxide layer
 - 304 First zinc oxide layer
 - 305 First photovoltaic element

- 306 Transparent electrode
- 401, 403 Short circuit in the second photovoltaic element
- 402 Short circuit in the first photovoltaic element
- 5 500 Semiconductor deposited film forming apparatus
 - 501 Load chamber
 - 502 Chamber for n-layer
 - 503 Chamber for i-layer of microcrystalline silicon
 - 504 Chamber for i-layer of amorphous silicon
- 10 505 Chamber for p-layer
 - 506 Unload chamber
 - 507, 508, 509, 510, 511 Gate valve
 - 512 Heater for heating microcrystal i-layer of substrate
- 15 513 Plasma CVD chamber for microcrystal i-layer
 - 514 Heater for heating n-layer of substrate
 - 515 Plasma CVD chamber for n-type layer
 - 516 Heater for heating i-layer of amorphous silicon of substrate
- 20 517 Plasma CVD chamber for i-layer
 - 518 Heater for heating p-layer of substrate
 - 519 Plasma CVD chamber for p-layer
 - 520 Holder transporting rail
 - 600 Sputtering chamber
- 25 601 Substrate holder
 - 602 Gas inlet tube
 - 603 Heater

- 604 Zinc oxide target
- 605 DC power source
- 606 Earth shield

[Name of the Document] Abstract

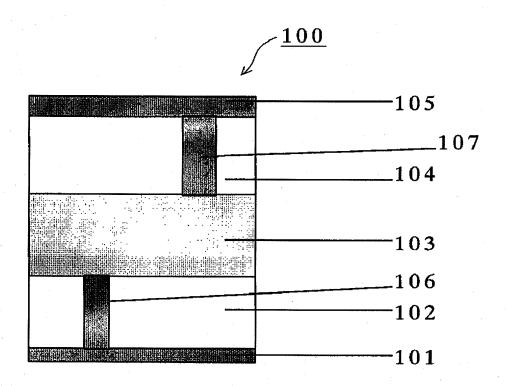
[Problem(s)] It is to provide a stacked photovoltaic element exhibiting a high conversion efficiency

- 5 realized by producing large photocurrent without causing decreased electromotive force.
 - [Means for Solving the Problem(s)] A stacked photovoltaic element comprising a plurality of unit photovoltaic elements each composed of a pn- or pin-
- junction, connected to each other in series, characterized in that a zinc oxide layer is provided at least one position between the unit photovoltaic elements, and the zinc oxide layer has resitivity varying in the thickness direction.
- 15 [Elected Drawing] Fig. 3

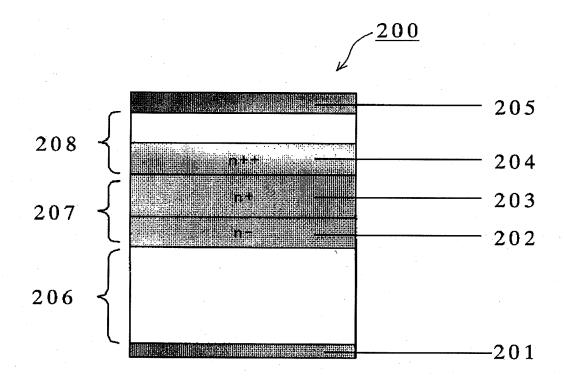
【書類名】

図面 [Name of Documents] Drawings

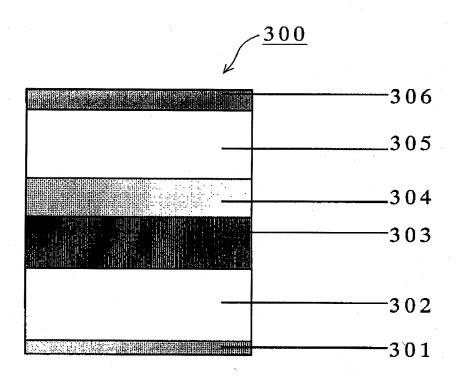
【図1】 下ig. 1



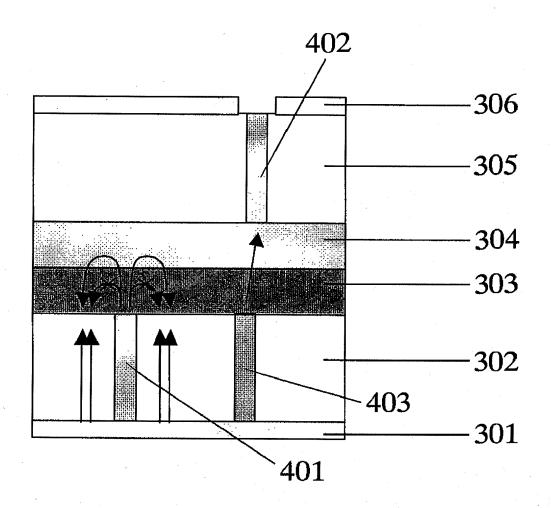
【図2】 Fig. 2



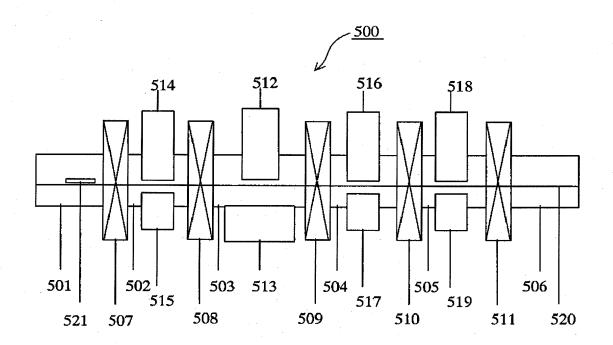
【図3】 Fig. 3



【図4】 Fig. 4



【図5】 Fig. 5



[\(\mathbb{Z}\)6] \(\tau_i, \quad 6\)

